COKING PROBLEMS ASSOCIATED WITH HYDROCARBON CONVERSION PROCESSES

R. Terry K. Baker
Catalytic Materials Center, Materials Research Laboratory,
The Pennsylvania State University, University Park, PA 16802

ABSTRACT

The understanding of the factors controlling the deposition of carbonaceous solids resulting from the decomposition of hydrocarbons over hot metal surfaces has a considerable impact on a number of commercial processes including, catalytic steam reforming of methane, steam cracking of paraffinic feed stocks and systems involving carbon monoxide disproportionation reactions. The potential for carbon formation exists in any system in which hydrocarbons undergo thermal decomposition and it is well known that certain metals can increase the overall rate of this process by catalyzing the growth of filamentous and graphitic types of deposit. The highest catalytic activity for carbon deposition is exhibited by iron, cobalt and nickel, and alloys containing these metals. In this paper a review of the information obtained from the use of a combination of controlled atmosphere and high resolution transmission electron microscopy techniques to study the dynamics of carbon deposition arising from the metal catalyzed decomposition of hydrocarbons will be presented.

INTRODUCTION

A number of review articles have highlighted the complex nature of carbon deposits produced during hydrocarbon decomposition reactions [1-6]. The major constituents of a typical carbonaceous solid that might accumulate on a metal surface, either in the form of a tube or as a particle dispersed on a support medium, can be divided into three main classes: amorphous, filamentous and graphitic platelets. During a traditional routine analysis of a contaminated reactor vessel or a spent catalyst, these three forms of carbon would not be necessarily distinguished, but merely referred to collectively as "coke". Available evidence indicates that the amorphous carbon component is formed via condensation and polymerization reactions and this material originates from thermal processes. It is conceivable that a significant amount of hydrogen is incorporated in the deposit, however, as the temperature is raised dehydrogenation reactions will tend to reduce the hydrogen content. There is now a general consensus that the formation of the filamentous and graphitic forms of carbon require the participation of a catalytic entity that usually operates in a particulate form.

The mechanism commonly accepted to account for the observed characteristics of the steady-state growth of carbon filaments from the metal catalyzed decomposition of carbon-containing gases involves the following steps [7-9]:

(a) adsorption of reactant gas molecules at particular faces of the metal particle followed by decomposition to generate carbon species, and

(b) dissolution in and diffusion of carbon species through the metal particle to a different set of faces that favor precipitation of carbon in the form of a fibrous structure.

The latter set of faces control not only the degree of crystalline perfection of the deposited carbon filament, but also the conformational characteristics of the material. A consequence of this phenomenon is that certain metal faces will remain free of deposited carbon and therefore, available for continued reaction with the hydrocarbon.

While the rudiments of the formation of the graphite platelet deposit have not received the same attention as that devoted to the growth of filamentous carbon it is probable that many of the steps outlined above are also operative in the formation of this type of carbon. Nolan and coworkers [10] reported that graphite, in the form of a shell structure surrounding a metal particle core, was the exclusive type of deposit produced from a carbon monoxide reactant containing no added hydrogen. They observed that the limiting thickness of the graphite shells was about 30 layers, and that this parameter was dependent on the lifetime of the metal catalyst particles. Based on these findings, they argued that the growth of graphite layers did not occur via a mechanism that involved precipitation of carbon from the surface of the metal. These claims were in direct conflict those of earlier studies [11-13] that clearly demonstrated that precipitation was the key step in the formation of graphite.

CHARACTERIZATION OF CARBON DEPOSITS

Before proceeding further it is worthwhile to consider the relative rates of the formation of these three types of carbon as a function of reaction temperature and the plot, Figure 1 provides an indication of the typical composition of the "coke deposit" that one might

expect under various conditions from the interaction of a metal with a hydrocarbon environment. It can be seen that for reactions conducted between 400 to 650°C, the composition of the deposit will tend to consist of a large fraction of filamentous carbon and when such reactions are allowed to proceed for a prolonged period of time the fibrous structures will undergo a thickening process due the accumulation of an amorphous carbon coating. A further ramification of this sequence of events is that the growth of filamentous carbon on a reactor tube wall provides a high surface collection site for trapping the amorphous carbon constituent and this combination effectively produces a very strong composite material. At temperatures in excess of 750°C the contribution of carbon filaments to the overall deposit will tend to decline while that of amorphous carbon will exhibit a steady increase and the emergence of the graphite platelet constituent will become evident.

The details of the growth kinetic aspects of individual carbon filaments was elucidated a number of years ago from quantitative analysis of the dynamic events captured on video-tape from experiments performed in the controlled atmosphere electron microscope. From measurements of the rate of increase in length of similar width structures as a function of temperature it was possible to evaluate apparent activation energies for the growth of filaments from various metal catalysts. The important aspect to emerge from this exercise was that from the accumulated data Baker and coworkers [7] were able to develop a mechanism that accounted for several of the growth characteristics and also established that the rate controlling step in the process was carbon diffusion through the catalyst particle. In more recent years [14-17] it has been recognized that the structural perfection of the deposited carbon solid is a parameter that is governed by the nature and shape of the catalyst particle and crystallographic orientation of the precipitating faces as shown schematically in Figure 2a-2c. In addition, symmetrical diffusion of carbon species through the particle will give rise to a relatively straight structure. In contrast, when certain additives are present in the metal particle the diffusion characteristics are modified and this factor causes a non-balanced process that results in the formation of coiled structures.

METHODS OF INHIBITING CATALYTIC CARBON FORMATION

The realization that the chemical and physical nature of metal particles plays a key role in catalyzing the growth of the filamentous form of carbon and that this material is also responsible for providing a very efficient method of trapping other types of deposit has lead to a number of approaches designed to inhibit its formation. These methods have tended to fall into the categories of either coating treatments of the metal surface with inert materials or the addition of selected compounds to the gas phase that might be expected to poison the activity of the metal towards catalytic carbon formation. From a consideration of the investigations that have been carried out, it is possible to establish a classification for the roles of various additives on the inhibition of filamentous carbon growth [18].

(a) There are some materials that merely provide a physical barrier towards hydrocarbon adsorption and subsequent decomposition on the metal surface, but during repeated temperature cycling tend to spall and the coating loses its effectiveness. e.g. Al_2O_3, B_2O_3

(b) Other additives reduce carbon solubility in the metal catalyst, but have no effect on the carbon diffusion characteristics through the particle, e.g. MoO_3, WO_3 and Ta_2O_5

(c) There are cases where an additive can reduce both the solubility of carbon and its diffusion through the metal particles, e.g. SiO_2, and finally,

(d) There certain electro-negative elements that when introduced into the either as a pre-treatment or on a continuous basis, effectively modify the chemistry of the metal surface so that it can no longer function as a catalyst to dissociatively chemisorb the carbon-containing gas molecules, e.g. sulfur, phosphorus and halides.

ISSUES THAT NEED TO BE ADDRESSED WITH REGARD TO CATALYTIC CARBON DEPOSITION

When one examines the ramifications of filamentous carbon formation under conditions where such structures are produced on either a metal tube surface or on isolated metal particles supported on a carrier material there are a number of questions that at point in time have not been satisfactorily answered. It is not clear whether these fibrous structures merely function as a high surface collection site or if they perform a catalytic function in being able to promote the formation of amorphous carbon from interaction with gas phase reactants. One might also offer a counter argument that an enhancement in the formation of the amorphous carbon component could effectively form a physically blockage of the metal surface, thereby inhibiting its catalytic action with respect to growth of filamentous carbon. A further factor could have a significant impact on the particular hydrocarbon conversion process is the possible impact of the fibrous material on the mass flow of reactants under either gas or liquid phase conditions.

Other potential problems center around the identity and fate of metal particles that perform the catalytic function. While we have established which metals are the most catalytically active for the growth of filamentous carbon there are still unsolved mysteries surrounding the precise influence of small amounts of a second metal. The addition of very small amounts of silver, tin, or copper to nickel, iron and cobalt can result in a dramatic increase in the ability of the ferromagnetic metal to catalyze the growth of filamentous carbon. Under a typical commercial reactor condition one must be aware that the likelihood of introducing impurity species into a host metal is extremely high and this behavior could have catastrophic effects on the carbon deposition process. Finally, it is imperative that we are able to determine the influence, if any, of the metallic inclusions in the deposit on the subsequent decoking step. It would be pertinent to ask whether such species function as catalysts for the removal of carbon and under these circumstances what is the fate of the metal particles following the gasification reaction. The ramifications of the difference in behavior of metal particles associated with filamentous carbon during reaction in oxygen is depicted in Figure 3. In the case where the metal facilitates the removal of carbon the particle returns to the original location on the support medium. In contrast, where gasification proceeds without the participation of the metal, then there is a high probability will eventually be swept out of the system by the reactant gas stream. In this context it might be worthwhile in certain reaction systems to consider introducing additives during the decoking cycle that are known to be good catalysts for the carbon gasification step and that are either benign towards carbon deposition or can easily be removed prior to re-introduction of the hydrocarbon feed.

SUMMARY

In conclusion, it is clear that significant improvements have been made over recent years with respect to controlling the rate of carbon deposition in a selected number of systems. There is, however, a strong case to be made for attention to be focused on some of the fundamental aspects of this problem so more effective treatments can be developed. One must be mindful that such treatments may not have universal application and it is necessary to be cognizant of a number of prevailing factors when one is attempting to design an inhibition package for a given system. These aspects include, the nature of the metal surfaces and the reactant molecules, the temperature at which contact between these components will occur and some knowledge of the identity and concentration of possible contaminants that may be present, particularly in the gas phase.

ACKNOWLEDGMENTS

REFERENCES

1.   Hofer, L. J. E., in "Catalysis", Vol. 4 (P. H. Emmett.ed.) Reinhold Publishing Co., New York, 1956, p.373.
2.   Palmer, H. B., and Cullis, C. F., in "Chemistry and Physics of Carbon", Vol. 1 (P. L. Walker, Jr. ed.), Marcel Dekker, New York, 1965, p. 265.
3.   Rostrup-Nielsen, J. R., "Steam Reforming Catalysts", Tekorisk Forlay A/S, Danish Technical Press, Inc. 1975.
4.   Trimm, D. L., Catal. Rev.-Sci. Eng. 16, 155 (1977).
5.   Baker, R. T. K., and Harris, P. S., in "Chemistry and Physics of Carbon", Vol. 14,(P. L. Walker, Jr. and P. A. Thrower, eds.), Marcel Dekker, New York, 1978, p. 83.
6.   Bartholomew, C. H., Catal. Rev.-Sci. Eng. 24, 67 (1982).
7.   Baker, R. T. K., Barber, M. A., Feates, F. S., Harris, P. S., and Waite, R. J., J. Catal. 26, 51 (1972.
8.   Lobo, L. S., Trimm, D. L., and Figueiredo, J. L., in "Proc. 5th Intern. Congr. Catalysis, Palm Beach, 1972" (J. W. Hightower, ed.) Vol.2, North-Holland, Amsterdam, 1973, p.1125.
9.   Alstrup, I., J. Catal. 109, 241 (1988).
10.   Nolan, P. E., Lynch, D. C., and Cutler, A. H., Carbon 32, 477 (1994).
11.   Presland, A. E. B., Roscoe, C., and Walker, P. L., Jr., 3rd.Conf. Ind. Carbon and Graphite, London, 1970.
12.   Baker, R. T. K., Feates, F. S., and Harris, P. S., Carbon 10, 93 (1972).
13.   Baker, R. T. K., Harris, P. S., Henderson, J., and Thomas, R. B., Carbon 13, 17 (1975).
14.   Audier, M., Oberlin, A., Oberlin, M., Coulon, M., and Bonnetain, L., Carbon 19, 217 (1981).
15.   Yang, R. T., and Chen, J. P., J. Catal. 115, 52 (1989).
16.   Kim, M. S., Rodriguez, N. M., and Baker, R. T. K., J. Catal. 134, 253 (1992).
17.   Rodriguez, N. M., Chambers, A., and Baker, R. T. K., Langmuir 11, 3862 (1995).
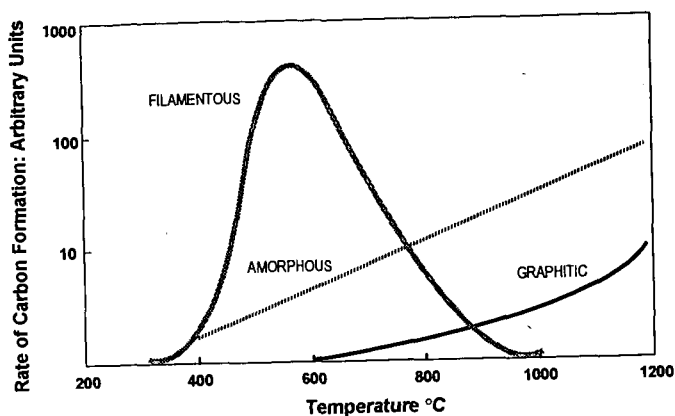18.   Baker, R. T. K., and Chludzinski, J. J., J. Catal. 64, 464 (1980).

Figure 1. Relative rates of formation of the three types of carbon deposit as a function of reaction T.
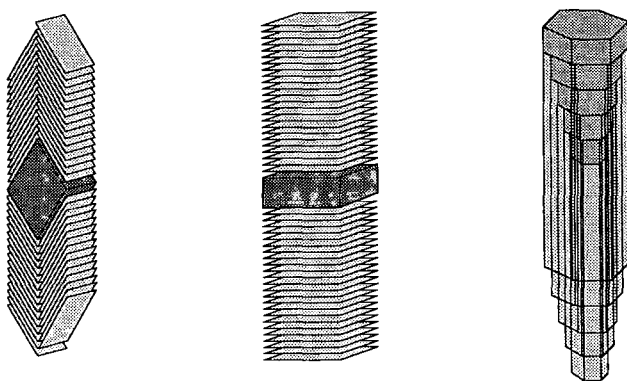

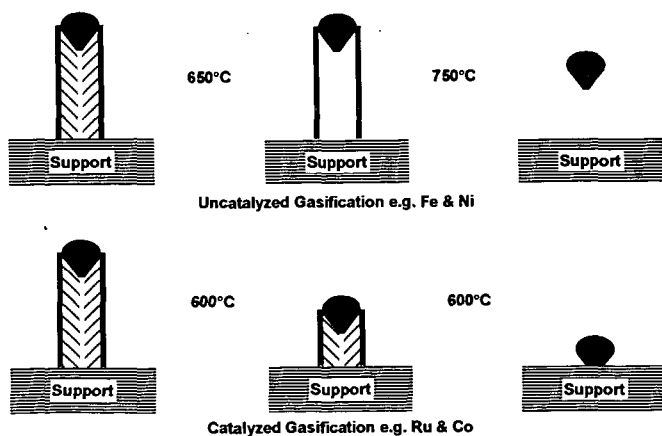Figure 2. Schematic representation of different types of filamentous carbon structures

Figure 3. Fates of catalyst particles during gasification of filamentous carbon in O_2